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The main goals in the previous grant period have been to develop new, more effective methods for performing accurate ab initio electronic structure calculations and to use these methods for the prediction of molecular structure, bonding and reactivity, especially for main group species and reactions of interest to the Air Force. From the theoretical point of view, the principle accomplishments have been extensive development of approaches and codes for performing electronic structure calculations in parallel, continued development of methods for interfacing electronic structure calculations with dynamics, initial studies of the possibliity of splicing together different levels of electronic structure theory, and the development of a new model for treating solvation. Applications have ranged from the development of very accurate and extensive potential energy surfaces for A +HB reactions (to interface with the experiments f Neumark and Zare) to the role of catalysts in the hydrosilation reaction to extensive studies of reactions involved in both main group and transition metal chemical vapor deposition (CVD) to broad-based studies of cage molecules (using our new parallel capabilities) that are potential precursors for new materials, electronic and optical devices, and catalysts. A new area that we have entered into is a series of systematic calculations on transition metal (TM) -main group (MG) compounds and their reactions, with particular emphasis on their roles as catalysts and in such inportant areas as CVD.

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AFOSR REPORT
THEORETICAL STUDIES OF SILICON AND RELATED ELEMENTS

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The main goals in the previous grant period have been to develop new, more effective methods for performing accurate *ab initio* electronic structure calculations and to use these methods for the prediction of molecular structure, bonding and reactivity, especially for main group species and reactions of interest to the Air Force. From the theoretical point of view, the principle accomplishments have been extensive development of approaches and codes for performing electronic structure calculations in parallel, continued development of methods for interfacing electronic structure calculations with dynamics, initial studies of the possibility of splicing together different levels of electronic structure theory, and the development of a new model for treating solvation. Applications have ranged from the development of very accurate and extensive potential energy surfaces for A +HB reactions (to interface with the experiments of Neumark and Zare) to the role of catalysts in the hydrosilation reaction to extensive studies of reactions involved in both main group and transition metal chemical vapor deposition (CVD) to broad-based studies of cage molecules (using our new parallel capabilities) that are potential precursors for new materials, electronic and optical devices, and catalysts. A new area that we have entered into is a series of systematic calculations on transition metal (TM) - main group (MG) compounds and their reactions, with particular emphasis on their roles as catalysts and in such important areas as CVD.

In the following pages, we summarize the progress of our recent AFOSR research, starting with theory/model developments and followed by applications.

I. MODEL DEVELOPMENT

Calculations of accurate potential energy surfaces (PES's) for molecular isomerizations and dissociations and chemical reactions are highly compute-intensive, frequently requiring the use of very large basis sets and multi-reference wave functions. Multi-reference wave functions are especially critical when more than one electronic state is involved in the calculation. Therefore, a major effort in our group has been to increase the efficiency of the calculations by developing electronic structure codes that may be used on parallel computers.

Our philosophy has been to make the codes as general and (therefore) as portable as possible, so that they may be used in virtually any parallel environment. The platform used for the

parallel developments is GAMESS[1] [General Atomic and Molecular Electronic Structure System]. As developed in our laboratory, parallel GAMESS can be run using a modest number of workstations. A one-word option optimizes the performance, depending on whether several workstations of the same type or with different capabilities are being used. The same code may be run on larger "massively parallel" computers. For example, parallel GAMESS is generally available on the 16 node Intel iPSC 860 computer at Kirtland AFB, on the 512 node Intel Delta at CalTech, on the 512-node Connection CM-5 at the AHPC (University of Minnesota), on the Intel Paragon at the San Diego Supercomputer Center and the IBM SP2's at the Cornell Supercomputer Center and the Maui Center. At the other end of the scale, a version of GAMESS is now running on 486 computers (which may also be hooked in parallel) under a shareware version of UNIX.

The currently distributed version (at no charge to users) includes parallel capability for essentially all types of wave functions, including Hartree-Fock (RHF, UHF, ROHF) and two-configuration (TCSCF or GVB) wave functions, and their associated analytic gradients[1], analytic hessians[2], and MCSCF and CI wave functions[3]. This means that geometry optimizations, transition state searches, and reaction path following can all be performed using the parallel algorithms. For the SCF levels of theory, the scalability of the calculations with increasing numbers of nodes is close to ideal (100%) for up to 16 nodes, as long as the size of the application is increased as the number of nodes is increased. Very little efficiency is lost through 32 nodes, and significant speedups are obtained even with 256 nodes. The hessian and MCSCF algorithms have not been as extensively tested, but preliminary indications are that the scaling will be very good. The next steps will be to develop parallel MP2 gradient codes. We have also initiated the implementation of a density functional code.

To study large compounds, novel ways must be developed to perform reliable calculations. One can, in principle, splice together two different levels of *ab initio* wavefunctions, *ab initio* with effective core potentials, *ab initio* with semi-empirical, etc. We have explored splicing together STO-3G with 6-31G(d) for a series of small molecules[4]. The procedure works amazingly well, as long as the minimal basis set is placed sufficiently far away from the functional group. We are now proceeding to the much more challenging process of splicing *ab initio* with semi-empirical calculations.

Closely connected to our developments of new approaches for treating larger systems is the development of new solvation models, in collaboration with Professor Walter Stevens at CARB. The method treats the solute (which could be a molecule, areacting system, or a reacting system

surrounded by a small number of solvent molecules) using *ab initio* wave functions. The solvent is treated using frozen solvent molecules (effective fragments) that are described by a model potential that includes electrostatic, polarization, and exchange repulsion terms. This model potential is obtained by fitting to *ab initio* potential energy surfaces and contains response functions to the *ab initio* potential that allow the two parts to be mutually iterated to self-consistency. The derivations for the fragment-solute and fragment-fragment interaction terms and gradients have been derived and coded, as have the equations that allow us to follow minimum energy paths for reactions that occur in solution. The model is now undergoing extensive testing.

The study of PESs for chemical reactions often involves more than one electronic state. When this occurs, it is necessary to determine the spin-orbit coupling among these states. We have devised a general scheme for directly calculating the one-electron matrix elements and then using these results to parametrize the two-electron contributions, all using the GAMESS MCSCF programs. The predictive ability of this method for diatomics and small polyatomic molecules is quite good[5]. The next step is to develop general algorithms to permit the calculation of the full spin-orbit matrix elements.

II. STRAINED RING COMPOUNDS:MATERIALS PRECURSORS

Sita et al. found that while it is not difficult to synthesize 1,1-difluoro-1-stannacyclobutane, they are unable to isolate the analogous 3-membered ring. The question is whether this occurs because (a) the 4-membered ring is kinetically more stable, (b) the 3-membered ring is not a minimum on the potential energy surface (PES) or (c) the 3-membered ring is thermodynamically disfavored. Another question is whether stannacyclopropene is a weakly bound π complex. We have performed *ab initio* calculations[6] on the reactions EX_2 + HCCH -> metallocyclopropene, with E=C,Si,Ge,Sn and X=H,F. Since CH_2 is rather unstable, one expects a very exothermic reaction with little or no barrier for E=C and X=H. SnF_2 is expected to be quite stable, so a less exothermic reaction with a larger barrier is expected. As long as X=H, all reactions are quite exothermic with no barrier, although the exothermicity decreases as E gets heavier. When F replaces H, there is a large decrease in exothermicity. The reaction for E=Sn and X=F is predicted to be *endo*thermic and to have a substantial barrier. This explains the difficulty in preparing the 3-membered ring. No evidence is found that the bonding in these compounds can be described as π complexation.

A systematic analysis has been carried out on two series of compounds whose parents are

disiloxane (H_3Si-O-SiH_3) and disilane (H_3Si-SiH_3). For each series a H atom on each Si is successively replaced by a bridging O[7]. The final compound in each series has three oxo bridges. In the first series this produces a bicyclopentane analog, while in the second series one obtains an analog of [1.1.1]propellane. The molecules in the second series with two and three oxo bridges are diradicals with little bonding between the bridgehead Si atoms. So, these species must be described by multi-configuration (MC) wavefunctions, and the conclusions drawn from previous calculations are unreliable.

It was discovered in the 1980's that the cage compounds known as cyclophanes can be synthesized such that the bridgehead hydrogen points inside the cage, toward the *trans*-annular benzene ring (endo position), rahter than outside (exo position). Professor Damrauer (University of Colorado-Denver) attempted to synthesize the analogous compound in which the bridgehead carbon is replaced by a hydrogen, in order to explore the potential use for such compounds as materials precursors. However, these attempts were not successful. In an effort to understand why the endo silacyclophanes could not be made, we performed a series of calculations, making use of parallel GAMESS, to determine the preference for endo vs. exo, as a function of the nature of the bridgehead atom. It is found that when the bridgehead atom is C, the endo structure is preferred by about 13 kcal/mol, whereas the exo isomer is preferred by a huge 43 kcal/mol when the bridgehead atom is Si! The reason for this difference is that a C-H bond is polarized C(-)H(+), leading to a favorable electrostatic interaction between the positively charged H and the electron rich benzene ring. On the other hand, an Si-H bond is strongly polarized Si(+)H(-), leading to a repulsive interaction between an endo H and the benzene ring. This led us to propose increasing the size of the cage by one methylene group. Indeed, an expanded cage stabilizes the endo isomer of the silacyclophane by 40 kcal/mol, so that it is within 3 kcal/mol of the exo isomer.

Silatranes are well known to be important materials precursors, while phosphatranes are among the strongest bases known (and therefore important catalysts). Again using the parallel capabilities of GAMESS, we have performed an extensive study of both series of compounds. For the silatranes, we have discovered[54] that the fundamental nature of the *trans*-annular Si-N bonding is a dative interaction between the N lone pair and the positive Si. The often invoked three-center two-electron bond plays only a minor role. Although it usually assumed that the nature of the axial substituent has the greatest impact on the Si-N bond, we find that the nature of the adjacent (equatorial) atoms is more important. In fact, the most stable silatranes appear to be those in which these equatorial atoms are nitrogens (azasilatranes). A simple self-consistent reaction field (SCRF) model has been used to interpret the experimentally observed large shortening of the Si-N *trans*-annular bond in the condensed phase. The silatranes have a very large

dipole moment, and this leads to a large electrostatic interaction with the solvent which in turn causes a large shortening of the bond. With regard to the phosphatranes[50], we have predicted the gas phase basicities as a function of the equatorial atoms and substituents on the phosphorus. Both the precdicted geometries and basicities are in excellent agreement with the available experimental data. In addition, we have predicted some species which should be even stronger bases than those which have already been prepared. Our experimental colleagues at Iowa State (Verkade group) are attempting to synthsize these compounds.

III. HYPERVALENT BONDING

Hypervalent compounds (in which the central atom is bound to more than the 'normal' number of ligands), especially those containing silicon, have been implicated in the mechanisms of a variety of reactions used for the synthesis of coatings, optical devices, and materials precursors. We have therefore continued our extensive analyses of hypervalent Si and related elements.

The reactions of $Si(OH)_4$ with several substrates have been studied[8], with 6-31G(d) geometry optimizations, followed by the evaluation of energetics at the MP2/6-31++G(d,p) level of theory, as well as with AM1. The first reaction of interest is

$$Si(OH)_4 + OH^- \rightarrow [Si(OH)_5]^- \rightarrow [Si(OH)_5]^{-\,\#} \rightarrow [Si(OH)_3O]^- + H_2O$$

The *ab initio* calculations predict the first step in the above process to be exothermic by nearly 60 kcal/mol. The transition state for water elimination lies 36 kcal/mol below separated reactants, and only 2 kcal/mol above the final products, so the entire process can occur with no additional energy. The AM1 calculations are in essential agreement with these findings. A Bader atoms in molecules (AIM) electron density analysis has been performed on each species in this process. Substantial intramolecular hydrogen bonding is found in the transition state, undoubtedly stabilizing this structure. The second sequence of reactions was designed to investigate the interactions of several neutral species, NH_3, H_2O, and HF with silicic acid. Ammonia and HF are potential drying agents in the sol-gel process. In each case, we find one or more minima corresponding to hypervalent silicon structures. For ammonia, a 6-membered ring structure, with a double hydrogen bond, is found to be about 4 kcal/mol more stable than the pentavalent $Si(OH)_4 \cdot NH_3$ structure. For water, two different hydrogen bonded minima are found. One of these is the 6-membered ring structure analogous to the one found for NH_3. This is predicted to be very slightly more stable than a structure with a single hydrogen bond. No minimum is found that corresponds to a pentacoordinated structure $Si(OH)_4 \cdot OH_2$. For HF, the weakest proton acceptor,only the 6-

membered ring double hydrogen bond structure is found. No minimum energy structure is found for the hypervalent species $Si(OH)_4$-FH.

A series of $SiX_6^{=}$ compounds (X = H,F,CH_3,OH,OCH_3) has been investigated with *ab initio* and AM1 calculations[9]. All of these species correspond to minima, with barriers to dissociation to SiX_5^{-}+ X^{-}. For X=F, the barrier to dissociation is > 20 kcal/mol with MP2/6-31+G(d). However, some of the molecules are unstable to autoionization; e.g, $SiH_6^{=}$ has a negative ionization potential. If enough electronegative ligands are placed around the Si, a positive IP is found; e.g, the IP of $SiF_6^{=}$ is > 1 eV. D orbitals play a minor role in the bonding of these compounds, and the Si center remains quite positive.

A series of neutral, hexacoordinated silicon compounds has been investigated as well[10]. Whereas the complex between SiF_4 and NH_3 is fairly weakly bound (8 kcal/mol), the hexacoordinated compound in which two ammonia molecules are placed in opposite positions is stable relative to SiF_4 + 2 NH_3 by 24 kcal/mol. This cooperative stabilizing affect is consistent with the notion of cooperative, "balanced" bonding in such species through the formation of three-center bonds. Water molecules are not as strongly bound in $SiF_4(H_2O)_2$, but a cooperative effect is found here as well. In contrast, CO compounds are very weakly bound to SiF_4 through the C atoms and not at all through the O atoms.

Silatranes have been prepared in both the gas phase and in crystalline form. Whereas the apparent Si-N dative bond is rather short in the X-ray structure, the gas phase distance is much longer. To determine if there is actually a bond in the latter, a combined *ab initio* and AM1 investigation was undertaken[11]. Although the Si-N distance does increase as each ethylenic bridge is added, the full silatrane maintains a Si-N bond. Squeezing the Si-N bond to the distance observed in the crystal only requires about 6 kcal/mol. Silatranes and their phosphorus and transition metal analogs are important precursors for materials, optical switches, and electronic devices. The phosphorus species in particular are among the strongest bases known and are therefore very important catalysts. Whereas the earlier calculations on the parent silatrane required semi-empirical geometry optimizations and only single point *ab initio* calculations, our recent development of parallel electronic structure codes will allow us to extensively explore the structure and reactivity of "atrane" compounds as a function of central, axial and equatorial atoms. This is discussed in more detail in the main body of the proposal.

To obtain an understanding of one of the basic differences in bonding between C and Si, *ab initio* calculations were performed on both MH_5 and MH_5^- compounds, with M = C, Si, Ge, Sn[12]. While C-H bonds exhibit shared interactions, M-H bonds (M = Si, Ge, Sn) are closed shell (ionic) in nature. There is substantially more electron density located at the C-H bond critical points than in the others. The H in the C-H bonds withdraws negligible electron density from C, but for the heavier systems, the H withdraws a significant amount of electron density from M. SiH_5^- is more stable energetically than SiH_5 because the axial and equatorial H's are stabilized to a greater extent than the Si is destabilized, and because the Si-H bonds in the anion are more ionic than the Si-H bonds in the radical. Similar results are found for Ge and Sn. On the other hand, the C destabilization upon CH_5^- formation is greater than the stabilization of the H's. So CH_5^- is less stable than CH_5.

Hypervalent bridge compounds with the general structure $[XSiR_3\text{-}Y\text{-}SiR_3X]^m$, with m=0,-1, have been implicated in various mechanisms for organosilicon reactions. We have undertaken a series of calculations on the anionic compounds with R = H, X = H or F, and Y = H, CH_3, NH_2, OH, F[13]. The nature of the substituent X has a profound impact on the stability of these bridge compounds relative to $SiH_3X + SiH_3XY^-$. When X = H, the bridge compounds are only marginally stable, whereas, the stability is as large as 40 kcal/mol for X = F. When X = F, the order of stability for Y is NH_2 > OH > F,H >> CH_3.

The anion $[(CH_3)_2AlO]^-$ was prepared in a flowing afterglow selected ion flow tube (FA-SIFT). In addition, acidity studies coupled with thermodynamic analyses have established that the conjugate acid of $[AlO]^-$ is AlOH, rather than HAlO. Companion *ab initio* calculations have been performed to (a) determine the gas phase acidities and heats of formation of HAlO and AlOH and (b) study the reaction of trimethylaluminum with OH^-.[14] Using G1 theory, it is shown that, in agreement with the experimental observations, the AlOH isomer is more than 40 kcal/mol lower in energy than HAlO. The reaction of trimethyl aluminum with hydroxide is completely analogous with the similar reaction of tetramethylsilicon studied earlier. The association reaction to form $[(CH_3)_3AlOH]^-$ is predicted to be downhill by 83 kcal/mol, at the MP2/6-31++G(d,p)//SCF/6-31G(d) level of theory. The preferred elimination channel from the aluminate is overwhelmingly that of methane loss. The transition state for this elimination is found to be 35 kcal/mol below the initial reactants, and it is found to resemble the analogous elimination transtion state for the corresponding siliconate: one finds a dissociative anionic proton transfer, with the transition state

resembling a leaving CH_3^- group which abstracts a proton as it departs. The elimination of water is a much higher-energy process.

IV. THERMOCHEMISTRY

Using homodesmic reactions, heats of formation have been predicted for all methylated disilanes[15]. This is the first consistent, systematic prediction for these compounds, experimental or theoretical, and provides an important data base for Si thermochemistry. Several new experiments have been prompted by these results, resulting in excellent agreement between experiment and theory. The heats of formation of two prototypical double bonded species, silene and disilene, and their silylene isomers have been predicted using G1 theory[16]. This is the first experimental or theoretical systematic prediction for these compounds. These results are extremely important, because once the heats of formation for these protoytpes are established, homodesmic reactions may be used to predict the thermochemistry of substituted compounds. We have now completed a systematic investigation of the heats of formation for all methyl-substituted silenes and disilenes[17]. As discussed in the main body of the proposal, a major part of our new effort will be to make use of multi-reference methods and extended basis sets to determine accurate thermodynamic properties for compounds containing metals in the first transition series.

V. Π Bonding.

Calculations were performed for prototypical high valent transition metal-alkylidene complexes, using ECP's for the metals[18]. The complexes include Group IVB (Ti, Zr, Hf) and Group VB (Nb and Ta) alkylidenes with hydride ligands, as well as models for the four coordinate olefin metathesis catalysts (Mo-, W-, and Re-alkylidenes). The predicted geometries are in good agreement with available experimental data. Localized MCSCF/CI orbitals are used to determine quantitatively for the first time, the principle resonance contributors to the M=C bonds. Resonance structures in which the C is at the negative end of the M-C bond contribute 50% to the total wavefunction, whereas those in which the bond is neutral contribute 45%. The wavefunctions are consistently dominated by five primary resonance contributors. One of these, never discussed before, corresponds to a dative C to M bond plus a covalent π bond and contributes roughly 33% of the total wavefunction. The effect of substituents on the C and ligands on the metal has also been examined[19]. Significant changes in the electronic structure are found to be effected in three ways: (1) The introduction of a highly electropositive substituent (e.g., Li) makes the M-C bond closer to a triple bond for the Ta alkylidenes. (2) A change in the metal atom, since the heavier

metals result in a much more nucleophilic carbon. (3) The use of π donor substituents increases the electrophilicity of the alpha C.

The nature of the M=Si double bond has been investigated with FORS MCSCF wavefunctions and ECPs[20]. The species studied were silylene complexes of the form $MSiH_2^+$ (M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni). The LMO/MCSCF/CI method was used to determine the main resonance contributors, and the results were compared with the C, Ge, and Sn analogues. Substantial changes are predicted in the electronic structure of the MSi bond upon moving from left to right across the periodic table. The MSi bonds are considerable weaker than their MC analogues; however, these bonds are stronger than the corresponding MGe and MSn bonds. Since examples of the latter species are known experimentally, the MSi species should be experimentally accessible.

The electronic structures of complexes arising from the formation of a double bond between a silylene and a high valent transition metal fragment have been investigated, using LMO/MCSCF/CI[21]. A prime motivation for this work was that complexes of this type, unlike their C analogs, have so far eluded attempts at experimental characterization. We have concluded that (a) It is necessary to include electron correlation to obtain an adequate description of the MSi π bond, whereas the σ bond is well represented at the Hartree Fock level; (b) The kinetic and thermodynamic stability increase when H ligands and/or substituents are replaced by electronegative species; (c) Group VB MSi bonds are more stable than their Group IVB analogues; (d) MSi double bonds are stronger when the MSi π bond is made more backbonding in nature. Strategies for designing stable M=Si species are suggested. The electronic structures of the transition metal-disilene complexes $MCl_2(Si_2H_4)$, with M = Ti, Zr, Mo, and W, and the complexes of disilene with $PtCl_3^-$ and $Pt(PH_3)_2$ have also been investigated[22].

The π bond energies in all group IV compounds with the formula $H_2A{=}BH_2$ (A,B = C, Si, Ge, Sn) have been investigated with SOCI/3-21G(d)//MCSCF/3-21G(d), by calculating the rotation barriers for these species[23]. The out-of-plane bend potential becomes flatter as A,B become heavier and the π bond energies appear to reach a lower limit of 20 kcal/mol, once A and/or B is Ge or Sn.

A series of calculations was performed to determine the effect of replacing carbon atoms with main group elements on the basic benzene structure, by investigating $E_3E'_3H_6$ compounds[24].

The sets of compounds had E, E' = C, Si, Ge, and E = B, Al, Ga; E' = N, P, As. It is found that for those species with alternating C or N, the planar benzene-like structure is a minimum on the potential energy surface. For all of the others, the planar structure has one or more imaginary frequency. Calculations are in progress to determine the minima on each of these surfaces.

VI. POTENTIAL ENERGY SURFACES AND DYNAMICS

The details of A + HB potential energy surfaces is essential for the development of an understanding of a variety of AFOSR-supported experimental studies (for example, the photodetachment experiments of Neumark). We have therefore embarked on a series of accurate calculations of such potential energy surfaces. The global PES for the reaction $O(^3P) + HCl \rightarrow OH + Cl$ has been investigated at the MP2/6-311G(d,p) level of theory[25]. The transition state is rather bent, in agreement with the experimental observation that the product OH is rotationally hot. The global PES has been scaled using known experimental data and then fit to an analytic form. This surface has been used to investigate the dynamics of the reaction using quantal close coupling methods[25]. Tunneling plays a very important role in determining the rates and branching ratios. The transition state for the Cl + HCl reaction is found to be nonlinear, albeit rather flat. It requires at least an MP2 or MCSCF+CI wavefunction to obtain a proper PES. This effort used MP2 and multi-reference CI wavefunctions to map the PES[26]. A large number of points on the PES have been obtained, and are now being fit to an analytical form, in preparation for an analysis of the dynamics of the reaction. Preliminary results suggest that an adequate treatment of the dynamics will require a detailed knowledge of the PES's for the excited π state, as well as the σ ground state. We have therefore been performing extensive MCSCF calculations on both the ground and excited state potential energy surfaces.

Pseudorotation in SiH_5^- has been investigated by following the minimum energy path (MEP) from the tetragonal transition state to the trigonal bipyramidal minimum, using MP2/6-31G(d,p) energies[27]. The reaction path hamiltonian was then determined. Using this RPH, we have predicted the rate of the pseudorotational motion at several temperatures using variational transition state theory (VTST) and the small curvature tunneling approximation. We are now in the process of fitting the PES to an analytic form, in preparation for investigating trajectories on this surface. A series of substituted pentacoordinated Si anions is being investigated in an analogous manner[28]. For SiH_4F^-, if correlated wavefunctions and/or extended basis sets are used, the equatorial isomer becomes a transition state. So the simple Berry notion of

pseudorotation is an over-simplification for complex species. Similar results are found for polysubstituted pentacoordinated anions. PH_4F is isoelectronic with SiH_4F^- and exhibits a pseudorotation surface which is similar to that of the anion[29]. For this molecule, the MEP and several associated paths have been followed to demonstrate that as one proceeds from the highest transition state (square pyramid) down to the lower energy transition state (equatorial), the imaginary frequency disappears before the new imaginary frequency (corresponding to the MEP leading from equatorial to axial) appears. This is expected to have a major impact on pseudorotational dynamics. The PES for PH_4F will be fit to an analytic form to study the dynamics of this process.

The foregoing results have propelled us to a systematic study of pseudorotation of $[SiX_nH_{5-n}]^-$ compounds, with X = F,Cl[30]. For n = 1,2, many of the structures expected based on a classic Berry model do not exist on the MP2/6-31++G(d,p) PES. For n = 3,4,5 the compounds behave in a more classical way, except that Cl^- tends to be rather weakly bound and frequently dissociative.

The effect of SiH_3, GeH_3, and SnH_3 groups on ethyl cation has been investigated using isodesmic reactions at the MP2/3-21G(d) level of theory[31]. The stabilization effect increases steadily as the group IV substituent gets larger. The predicted effect is not as dramatic as is observed experimentally, suggesting that there is an additional kinetic effect, so the next step is to determine the transition states and associated energy barriers. As a follow-up to this analysis, the effect of ß-silyl substitution on stabilization of singlet (relative to triplet) carbene has been investigated[32]. It is found that there is indeed such a ß-silicon effect, due to the ability of ß C-Si (or C-Ge) bonds to twist into a position that permits electronic back donation from the C-Si bond into the empty p orbital on the carbene carbon.

The potential energy surfaces for several reactions related to *chemical vapor deposition* have been analysed. A systematic analysis of all thermal decomposition paths for silanol has been carried out[33]. Transition states and activation barriers for all reactions have been determined, as well as MEPs for all of the reactions which have transition states. Unlike all other such species studied to date, the 1,2-elimination of H_2 is competitive with the 1,1-elimination. In keeping with our increasing interest in transition metal CVD, analysis of the analogous potential energy for the Ti analog has just been initiated. In addition to its relevance to CVD, these calculations on Group IVB metal oxides (performed with extended all-electron *ab initio* basis sets and correlated wave

functions) interfaces with the AFOSR-funded experiments of Damrauer and Bierbaum.

The decomposition PES from bridged disilyne to $Si_2 + H_2$ has been explored, using a full valence, state-averaged MCSCF calculation, followed by first order configuration interaction for energetics[34]. It is predicted that the energy increases monotonically along the dissociation path, with no intervening barrier. The insertions of CH_2 and SiH_2 into the X-Y bonds of ethane, methylsilane, and disilane have been investigated and compared with the analogous insertion into the X-H bonds[35]. Insertions into the X-Y bonds have much larger barriers than the X-H insertions for each bond type (i.e., C-C vs. C-H; Si-Si vs. Si-H). Otherwise, the barrier heights appear to correlate more with bond length than with bond strength, since there is a steady increase in barrier height upon going from C-C to C-Si to Si-Si. When the X-Y bond is in a strained environment, such as the C-C bond in cyclopropane, the insertion barrier is dramatically reduced.

The insertion of SiH_2 into water was studied in this laboratory several years ago. Recent experiments by Walsh and co-workers suggest that the height of the barrier separating the addition complex H_2Si---OH_2 from silanol is much lower than that predicted by the earlier calculations. We have probed this PES with much improved wavefunctions[36] and verified the earlier predictions. Since the actual experiments were performed on dimethylsilylene, the calculations were repeated on the substituted species. The effect of the methyls bring theory and experiment into acceptable agreement (within 2 kcal/mol).

Recent experiments indicate a "negative activation energy" in the insertion of SiH_2 into SiH_4 to form disilane. This suggests the existence of a long-range minimum on the PES. Using MP2/6-311G(d,p) calculations, we have found a SiH_2-SiH_4 complex on the Si_2H_6 PES[37]. A transition state has been found that corresponds to a very small barrier separating the complex from product disilane. When zero point vibrational corrections or higher level correlation corrections are added, the barrier disappears. So, at best, there is a very flat region in this area of the PES. We are now examining this PES in greater detail, in order to understand the reaction and the related dynamics. Because of its importance to the chemical vapor deposition process, we have also investigated the insertion of SiH_2 into diatomic SiH[38]. Although the barriers to insertion for SiH_2 into SiH_4 and H_2 and for the insertion of CH_2 into SiH are all zero, a nonzero barrier of about 6 kcal/mol is predicted for this reaction at several levels of theory. This is in agreement with the recent experimental findings of Jasinski and appears to result from a combination of steric and electronic effects.

Related to these insertion reactions are calculations on the addition of divalent silicon species to the ethylene double bond. Earlier calculations from this laboratory have found that the addition of SiH_2 to ethylene to form the three-mebered silirane ring occurs with no barrier. When chlorines are substituted for the hydrogens in silylene, we find a small (<5 kcal/mol) barrier for the addition[56]. In contrast, when highly electronegative fluorines are substituted, a very high barrier is found. These results have been interpreted in terms of the competing electrophilic vs. nucleophilic interactions between the silylene and ethylene as a function of substituent.

A study of methane elimination from Group IVB (M = Ti, Zr, Hf) amido complexes **1** (of significance in connection with chemical vapor deposition (CVD) of Group IVB nitrides) of the form $(H)_2M(NH_2)(CH_3)$ was carried out.[39] The two major goals of this research were to develop computational approaches for treatment of transition metal (TM) complexes and to understand the effects of modifying the chemical environment (i.e., metal, ligands, leaving group, substituents, geometry, etc.) on the elimination barrier. Lower elimination barriers will improve the ability to process materials at lower temperatures (which lowers manufacturing costs and improves surface morphology) and increase rates of deposition at a given temperature. This research provided the first test of the Stevens effective core potentials (ECP) for calculation of accurate energetics involving transition metal (TM) species. Previous research had shown that the Stevens valence basis sets are sufficiently flexible for geometry predictions. An RHF optimization/MP2 energy approach for calculation of methane elimination barriers (1) for **1** yielded good agreement ($\approx$ 6 kcal mol^{-1}) with those measured and *subsequently* communicated by Wolczanski.

$$L_nM(CH_3)(NH_2) \quad \text{-->} \quad L_nM{=}NH \quad + \quad CH_4 \qquad (1)$$

All experimental trends for a series of related compounds are reproduced.

Using *ab initio* calculations of the intrinsic reaction coordinate (IRC) for the α-elimination process, agostic interactions were shown to be important for the first time, as experimentalists have inferred. The agostic interaction was found to be essential for activation of the N-H bond and transfer of H to the CH_3 leaving group. This discovery has important ramifications for materials research, since it implies that CVD precursors with agostic interactions built in will lie further along the IRC (i.e., close to eliminated product) and will allow this reaction to proceed with a lower elimination barrier. Future research will probe this inference.

A study of small molecule elimination ($HX = H_2$, CH_4, SiH_4, NH_3, HCl) from group IVB imido complexes ($M(H)_2(X)(NH_2)$) allowed us to probe the nature of the leaving group on the elimination process.[40] The ancillary ligand was fixed at H since the previous study[39] showed the ancillary ligands to have minimal impact on the topology of the reaction surface. This research marks the first extensive use of parallel computing with GAMESS[1] for the study of TM reactivity. Parallel computing, particularly when combined with methodological advances such as effective core potentials, holds great promise for study of increasingly complex transition metal complexes. The leaving group (X) was found to have a profound effect on the geometry of the transition state (TS). Electronegative leaving groups (NH_2 and Cl) moved the TS for elimination earlier, i.e. closer to amido reactant. The notion of a "flexible" TS is consistent with recent experimental work by Wolczanski et al. for RH elimination from high-valent amido complexes, and challenge the accepted notion of a static, late TS for α-alkane elimination. This has important ramifications for design of CVD precursors.

A linear correlation was found between the calculated elimination barrier and the MH_t distance in the TS. A shorter MH_t distance in the TS (and thus a stronger interaction between these two atoms) was found to correlate strongly with a lower elimination barrier. Thus, electroneutral (H and Me) and electropositive (SiH_3) leaving groups were found to lead to the lowest elimination barriers. We are now following up this work to see how other factors affect MH_t interaction and its correlation with elimination barriers, to see if this can serve as a simple criterion for the rational design of CVD precursors that can be processed at lower temperatures.

The IRC for methane activation by $Ir(PH_3)_2(H)$ was calculated and compared to experiment. Analysis of the wavefunction along the IRC showed that although donation of electron density from methane to metal was essential for adduct formation, not until back donation to σ^*_{CH} increases is the C-H bond activated and cleaved. The electronic and molecular structure of the reacting system along the IRC was interpreted in terms of a two-stage mechanism: substrate to complex donation is important in the early part of the reaction (electrophilic stage), while complex to substrate backdonation is necessary later on (nucleophilic stage) for C-H scission. Low- and high-valent C-H activating complexes show similar topology in the early portion of the activation event; differentiation between oxidative addition and sigma-bond metathesis occurs at the point at which there is a shift from the electrophilic to nucleophilic stage of the reaction.

As one moves to study deposition of materials containing transition metals on the right side of the transition series, it becomes more critical to understand the effects of d orbital occupation on pathways of interest to CVD. A study of methane elimination from a d^2 W-amido complex was initiated to probe this question.[41] Calculated barriers for α-methane elimination from $M(OH)_2(NH_2)(CH_3)$ are 24.9 kcal mol^{-1} ($M = d^0$-Ti) and 31.8 kcal mol^{-1} ($M = d^2$-W); the Ti value is in good agreement with a recent experimental determination of the enthalpy of activation for methane elimination from $Ti(OSi')_2(NHSi')(CH_3)$, $\Delta H^{\ddagger}_{elim} = 20.4$ kcal mol^{-1}. The rough similarity in TS energies comes despite a big difference in driving force for alpha-methane elimination; the d^2-W reaction is exothermic by 23.4 kcal mol^{-1} while the Ti reaction is endothermic by 11.7 kcal mol^{-1}. Analysis of bond energy data for Cp_2MMe_2 ($M = d^0$-Ti and d^2-W) suggests that half this difference is due to a stronger Ti-CH_3 bond; there is no available data to compare π-bond strengths involving metals, so that future work will focus on the systematic computation of π-bond energies.

Given the growing importance of the lanthanides in advanced materials (e.g., high-temperature superconductors) it is imperative that computational approaches be developed to treat their chemistry. An effective core potential scheme for the lanthanides was derived[42] in collaboration with Dr. Walter Stevens (National Institutes of Standards and Technology). Calculated properties for atomic ions show little loss in accuracy for prediction of energies (≤ 3%) when compared to highly-accurate, all-electron, fully-relativistic Dirac-Hartree-Fock calculations, despite an order of magnitude reduction in computation times. The ECP scheme has been implemented in GAMESS[1].

Alkyl substitution has a significant effect on the gas phase acidities of hydrocarbons. The effect of analogous substitutions on the corresponding Si compounds is the source of some controversy among experimental groups, with some finding the same effect as in the C compounds and others seeing little or no effect. We have carried out MP4 calculations with very large basis sets on SiH_3OH, $MeSiH_2OH$, and $EtSiH_2OH$ and the corresponding deprotonated anions[43]. The calculations predict that these compounds have essentially the same gas phase acidities. Similar predcitions apply to the analogous S compounds, where the calculations have predicted a serious error in experimental results. Theory has been determined to be correct.

The gas-phase reactions of trimethylaluminates and a variety of acids were considered from both an experimental and theoretical perspective[44]. The experimental work involved product and

kinetic studies of ten aluminates, $[(CH_3)_3AlX]^-$. Both X and methyl cleavage are observed in these reactions. Since X cleavage occurs for several aluminates, in contrast to the thermochemical predictions of MP2/6-31++G(d,p) calculations, it is concluded that the reactions are kinetically controlled. Therefore, studies of the reaction paths for the reactions of $[(CH_3)_3AlX]^-$, X = F, OH, with HCl have been carried out. These calculations properly predict the observed cleavage results for X and methyl cleavage and give a qualitative interpretation of the reaction dynamics.

An analysis of the electronic structure of high-valent transition metal alkylidenes as models for olefin metathesis catalysts was performed with *ab initio*/ECP wavefunctions[45]. Of particular interest was the elucidation of the fundamental differences between those complexes known as the "Fischer" type $[MCl_2(Y)(CH_2)]$ and those complexes known as the "Schrock" type $[M(OH)_2(XH)(CH_2)]$. The effect on the bonding caused by modification of either the metal, ligands, or substituents was considered.

Damrauer and co-workers have studied the reactions of $HCSi^-$ with several neutral triatomic molecules. While reaction products are observed for the reaction with CO_2, COS, and SO_2, no reaction is observed with CS_2. A detailed analysis of the corresponding PESs was undertaken[46]. The first step established that linear $HCSi^-$ is the only minimum on that PES. All four reactions are overall exothermic. The most exothermic reaction is the one which is not observed experimentally suggesting a kinetic explanation. For each reaction, we find two cyclic intermediates. Yet another, zigzag minimum is found in in this valley. For all four reactions, no barrier is found in the exit channel; however, for the reaction with CS_2, a very large barrier is found in the entrance channel between the reactants and first cyclic intermediate. Since no such barrier is found for the other reactions, this nicely explains the experimental observations.

Some work has also been completed on reactions of cations. It is well known that cationic species are important in high energy CVD involving plasmas. We have therefore carried out[55] very acccurate calculations on the competing thermal decompostion mechanisms for $CH_3SiH_2^+$. Even though the most favorable thermodynamic product is CH_3Si^+, there is considerable production of $CH_2{=}SiH^+$, due to the relative barrier heights. That is, kinetics plays an important role in this mechanism. An unusual weakly bound complex has also been found on the potential energy surface, and this complex nicely explains the observed exchange reactions. We have also extensively mapped out the potential energy surface for the reaction of Si^+ with CH_3SiH_3.[47] This

reaction has been studied experimentally at both thermal energies and at a range of higher temperatures. The calculated surface is in excellent agreement with all experimental data. Those reaction mechanisms for which all barrier heights are below the energy of the initial reactants correspond to the observed products for the threshold experiments, while those mechanisms that require the trversal of higher barriers give rise to products that are seen only at higher impact kinetic energies.

We have reported the existence of bond stretch isomerism in any silabicyclobutanes in which the bridgehead atoms are silicons. We have now mapped out the MEP connecting the two isomers in the tetrasila case at the GVB/6-31G(d,p) level of theory, calculated the projected vibrational frequencies along the path and predicted the free energy path for the reaction[38]. The next step is to make use of variational transition state theory to investigate the dynamics and kinetics for the bond stretch isomerization reaction. An interesting feature of this investigation will be to ask how vibrational excitation effects the rate constants and tunneling probabilities. These calculations will be followed by analogous studies of $Si_nC_{4-n}H_6$, with n=1-3.

Three invited reviews have also resulted from our AFOSR-supported research. Two chapters will appear in ACS Symposium series monographs on parallel computing[51,52], while a third review summarizes our work on transition metal-main group chemistry.[53]

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POTENTIAL ENERGY SURFACES AND DYNAMICS FOR HIGH ENERGY SPECIES

REPORT ON PROGRESS

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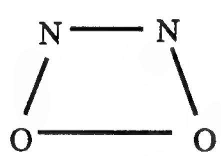
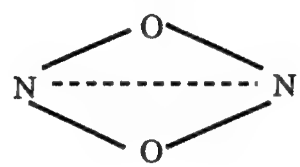
N_2O_2 AND RELATED SPECIES

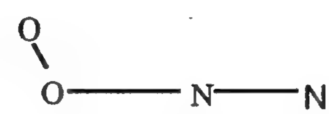
The stability of the asymmetric dimer of NO (a-N_2O_2: **3**) with respect to spin forbidden radiationless decay has been investigated[1]. The spin-allowed decay channel a-$N_2O_2(^1A')$ -> $N_2O(X^1\Sigma^+)$ + $O(^1D)$ is endoergic. However, the spin forbidden decay channel a-$N_2O_2(^1A')$ -> $N_2O(X^1\Sigma^+)$ + $O(^3P)$ is exoergic. Large-scale multi-reference CI wave functions, approximately 300,000 - 1,400,000 configuration state functions, based on double zeta plus polarization and triple zeta plus polarization bases sets were used to study this process. The minimum energy crossing point of the ground singlet state and the lowest excited triplet state was determined, as waa the interstate spin-orbit coupling. This electronic structure data was used in the context of a simple one-dimensional model to show that a-N_2O_2 is rapidly predissociated to $N_2O(X^1\Sigma^+)$ + $O(^3P)$. This means a-N_2O_2 is not a good HEDM candidate, despite the high energy content of this compound.



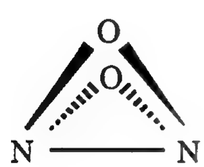
1 C_{2v}



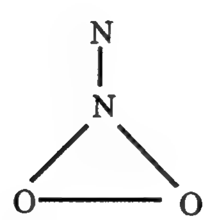
2 D_{2h}



3 C_s



4 C_{2v}



5 C_{2v}

Several other high energy isomers of N_2O_2 have been identified[2]. Two of these (**2**, **4**) may be thought of as bicyclo analogs of isoelectronic bicyclobutane. These two bicyclic isomers are predicted to be 63 and 66 kcal/mol above 2 NO, at the multi-reference CI level of theory, using the extended 6-

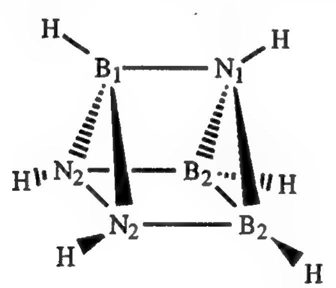
311+G(2d) basis set.

Because of the significant configurational mixing in these species, single-configuration based methods (e.g., perturbation theory methods or the G2 method) are found to be unreliable for prediction of relative energies. The next steps (already in progress) are to explore low-lying triplet states and the potential for nonadiabatic coupling between the ground and excited states, and to determine those parts of the potential energy surfaces that correspond to the dissociation of **1**, **2**, **4**, and **5** to 2 NO, $N_2 + O_2$, and other products.

Preliminary calculations[3] (at the SCF and second order perturbation level of theory) have revealed the possible existence of four high energy N_2O_3 isomers. The highest energy species has a structure very similar to that of [1.1.1]propellane, with which it is isoelectronic. Other promising structures are a distorted square pyramid and two structures containing four-membered rings. Based on the results summarized above for N_2O_2, reliable conclusions regarding the N_2O_3 potential energy surfaces will require the use of multi-configuration-based wave functions.

HIGHLY STRAINED RINGS

In the process of investigating the general effect of replacing some or all of the carbon atoms in benzene with hetero atoms, we have discovered several very high energy, nonplanar isomers of these compounds[4]. The most promising of these compounds have the formula $X_3N_3H_6$ with the heavy atoms arranged in a prismane structure (shown below for X = B):



Using second order perturbation theory and modest basis sets, the BN prismane is found to be more than 160 kcal/mol higher in energy than the planar benzene analog. Extensive searches are under way to determine pathways for the decomposition and isomerization of this high energy compound. Subsequent calculations will address the effects of substituents on the potential of this and related compounds (e.g., X = Al) as HEDM species.

We have previously reported the existence of bond stretch isomerism in any silabicyclobutanes in which the bridgehead atoms are silicons[5]. We have now mapped out the MEP connecting the two

isomers in the tetrasila case at the GVB/6-31G(d,p) level of theory, calculated the projected vibrational frequencies along the path and predicted the free energy path for the reaction[6]. We have found that the size of the groups attached at the bridgehead positions determine whether the short bond or the long bond isomer is lower in energy. When the bridgehead substituent is hydrogen, the highest levels of theory predict that the short bond structure may not even correspond to a minimum on the potential energy surface. On the other hand, the short bond structure is the lower energy isomer when bulky t-butyl groups are placed in the bridgehead positions. The next step is to make use of variational transition state theory to investigate the dynamics and kinetics for the bond stretch isomerization reaction. An interesting feature of this investigation will be to ask how vibrational excitation affects the rate constants and tunneling probabilities. A preliminary calculation of the specific impulse (I_{sp}) for silabicyclobutane, used as an additive to liquid hydrogen, suggests that this compound is a promising additive[6] (see discussion in main body of proposal). The relative stabilities of the long- and short-bond isomers clearly depend on the substituents placed on both the peripheral and bridgehead silicons, and the compound is easier to synthesize and stabilize when the hydrogen substituents are replaced with bulkier groups. It is therefore necessary to determine the structures, thermodynamic properties, and I_{sp}'s for a variety of substituted compounds, to assess their utility as HEDM species.

HYPERVALENT ANIONS

Pseudorotation in SiH_5^- has been investigated by following the minimum energy path (MEP) from the tetragonal transition state to the trigonal bipyramidal minimum, using MP2/6-31G(d,p) energies[7]. The reaction path hamiltonian was then determined. Using this RPH, we have predicted the rate of the pseudorotational motion at several temperatures using variational transition state theory (VTST) and the small curvature tunneling approximation. We are now in the process of fitting the PES to an analytic form, in preparation for investigating trajectories on this surface. A series of substituted pentacoordinated Si anions is being investigated in an analogous manner[8]. For SiH_4F^-, if correlated wavefunctions and/or extended basis sets are used, the equatorial isomer becomes a transition state. So the simple Berry notion of pseudorotation is an over-simplification for complex species. Similar results are found for polysubstituted pentacoordinated anions. PH_4F is isoelectronic with SiH_4F^- and exhibits a pseudorotation surface which is similar to that of the anion[9]. For this molecule, the MEP and several associated paths have been followed to demonstrate that as one proceeds from the highest transition state (square pyramid) down to the lower energy transition state (equatorial), the imaginary frequency disappears before the new imaginary frequency (corresponding to the MEP leading from equatorial to axial) appears. This is expected to have a major impact on pseudorotational dynamics.

The PES for PH_4F will be fit to an analytic form to study the dynamics of this process.

Many of the stationary points on the potential energy surfaces of NH_4^- and PH_4^- have now been identified at the MP2/6-311++G(d,p) level of theory, with single point energies being obtained with QCI/6-311++G(2df,2pd)[10]. Now, the remaining transition states are being identified and the minimum energy paths connecting the minima with each other and with XH_2^- + H_2 and with XH_3 + H^- (X=N, P) are being mapped out. Once these MEP's have been determined, the dynamics of the isomerizations and dissociations will be investigated using the methods discussed above for SiH_5^-.

MODEL DEVELOPMENT

Calculations of accurate potential energy surfaces (PES's) for molecular isomerizations and dissociations are highly compute-intensive, frequently requiring the use of very large basis sets and multi-reference wave functions. Multi-reference wave functions are especially critical when more than one electronic state is involved in the calculation. Therefore, a major effort in our group has been to increase the efficiency of the calculations by developing electronic structure codes that may be used on parallel computers. Our philosophy has been to make the codes as general and (therefore) as portable as possible, so that they may be used in virtually any parallel environment. The platform used for the parallel developments is GAMESS[11] [General Atomic and Molecular Electronic Structure System]. The currently distributed version (at no charge to users) includes parallel capability for all Hartree-Fock (RHF, UHF, ROHF) and two-configuration (TCSCF or GVB) wave functions, and their associated analytic gradients[11]. For these levels of theory, the scalability of the calculations with increasing numbers of nodes is close to ideal (100%) for up to 16 nodes, as long as the size of the application is increased as the number of nodes is increased. Very little efficiency is lost through 32 nodes, and significant speedups are obtained even with 256 nodes. The calculations can be performed on a variety of platforms, ranging from a small number of workstations of various types to massively parallel computers (e.g., Intel Delta at CalTech, Intel Paragons at San Diego Supercomputer Center and Wright-Patterson AFB, CM-5 at University of Minnesota).

The parallel capability has already had a major positive impact on our HEDM efforts, since the structure predictions and potential energy surfaces for both the inorganic prismanes and the substituted silabicyclobutanes would have been virtually impossible without the ability to perform these calculations in parallel. The prismane calculations have made use of RHF wave functions, using both all electron and effective core potential basis sets, while the silabicyclobutane calculations have been performed with TCSCF wave functions. A new algorithm for calculating analytic hessians in parallel

with a small number of nodes has been developed[12], and a parallel MCSCF code (the first to have been developed) is currently being tested[13]. The next steps will be to improve the MCSCF and analytic hessian parallel codes, implement parallel MCSCF gradients, and develop parallel MP2 and CI codes.

The study of PESs for chemical reactions often involves more than one electronic state. When this occurs, it is necessary to determine the spin-orbit coupling among these states. We have devised a general scheme for directly calculating the one-electron matrix elements and then using these results to parametrize the two-electron contributiions, all using the GAMESS MCSCF and CI programs. The predictive ability of this method for diatomics and small polyatomic molecules is quite good[14]. The next step is to develop general algorithms to permit the calculation of the full spin-orbit matrix elements.

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